

Computational Study on the Isomerization of Silacyclopropylidenoid Structures to Silaallenes

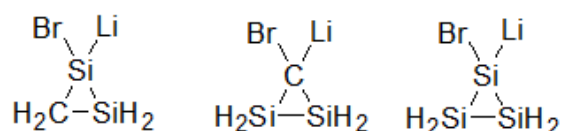
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The theoretical and experimental investigations of silaallenes have been attracting more and more interest in the past few decades because of their unique structures and the broad differences in their properties compared to the corresponding carbon compounds. [1-2]

More recently, theoretical calculations elucidated the ring-opening reactions of 1-bromo-1-lithiosilirane and 2-bromo-2-lithiosilirane to 2-silallene and 1-silaallene, respectively. The ring-opening of 1-bromo-1-lithiosilirane to 2-silallene can proceed in a stepwise fashion with the intermediacy of a free silacyclopropylidene. In contrast, the ring-opening of 2-bromo-2-lithiosilirane to 2-silallene can occur in a concerted fashion. [3]

Herein, we wish to report the results of DFT calculations on the isomerization of 1-bromo-1-lithiodisilirane, 3-bromo-3-lithiodisilirane, and 1-bromo-1-lithiotrisilirane, shown below to silaallenes. All theoretical calculations are carried out using the Gaussian03 suite of programs. [4]



On the basis of theoretical calculations we predict that the ring-opening reaction of 1-bromo-1-lithiodisilirane to 1,2-disilaallene can occur either in a concerted fashion or through a stepwise process with the intermediacy of a free silacyclopropylidene. In contrast, the ring-opening reactions of 3-bromo-3-lithiodisilirane and 1-bromo-1-lithiotrisilirane can occur in a concerted fashion. The activation energy barrier for the isomerization of 3-bromo-3-lithiodisilirane to the complex of 1,3-disilaallene with LiBr was determined to be only 2.6 kcal/mol at B3LYP/6-31+G(d,p) level, and the reaction is highly exothermic, which makes this reaction for a promising strategy for the synthesis of 1,3-disilaallenes. However, the energy barrier for the conversion of 1-bromo-1-lithiotrisilirane to trisilaallene is calculated to be quite high, 27.2 kcal/mol, and in this case the reaction is endothermic.

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[1] B. Eichler, R. West, *Adv. Organometal. Chem.* **2001**, *46*, 1–46.

[2] M. Karni, Y. Apeloig, J. Kapp, P. von, R. Schleyer, In the *Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; John Wiley & Sons: Chichester, **2001**; Vol. 3, pp 1-163.

[3] A. Azizoglu, C. B. Yildiz, *Organometallics*, **2010**, *29*, 6739–6743.

[4] M. J. Frisch, et al. Gaussian 03, Revision C.02; Gaussian, Inc.: Wallingford, CT, **2004**.